Photoisomerization of 9-tert-butylanthracene in polystyrene films under photoselection conditions. Consideration of molecular thermal rotation

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Abstract

Photoselection in thermoreversible photochemical reactions was theoretically and experimentally considered using the photoisomerization of 9-tert-butylanthracene in polystyrene as a model system. The influence of the thermal rotational mobility of the reactive molecules on the photoselection is discussed. A satisfactory agreement between the theoretically calculated kinetics of photoisomerization and the accumulation of dichroism and the experimental results is obtained. It is demonstrated that photo-oxidation in a polymer matrix corrupts the photoselection process.

Keywords: Photoisomerization; 9-tert-butylanthracene; Polystyrene films; Photoselection

1. Introduction

Reversible photoisomerization reactions in polymer matrices have been widely investigated in the development of photochromic systems [1]. Some have been found to induce dichroism of the optical absorbance on irradiation with polarized light [2–7].

During photoselection, irradiation with polarized light leads to the photochemical reaction of favourably oriented molecules only [8]. As a result, macroscopic optical anisotropy of the sample appears [8].

Photoselection in irreversible photochemical reactions in rigid media has been theoretically considered [8–10] and experimentally observed in a number of studies [11–14]. However, the results obtained are not applicable to the thermoreversible reactions of photoisomerization in polymers, as the reverse thermal reaction and thermal rotations of reactive molecules, observed in polymers [6,7], must be taken into account.

The purpose of this work was to investigate, experimentally and theoretically, the photoselection in thermoreversible isomerization reactions in a polymer matrix.

The photoisomerization of 9-tert-butylanthracene (TBA) to the Dewar isomer was chosen as a model system.

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TBA
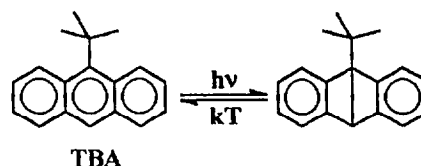
In the liquid phase, direct photoisomerization and reverse thermal isomerization are observed [15–17]. Linear dichroism in the optical absorption of TBA has been found previously in polystyrene films on irradiation with polarized light [6].

2. Experimental procedures

A solid polystyrene (PS) film doped with TBA ($(0.8–9) \times 10^{-3}$ M) (thickness, approximately 200 μm) was used. The films were prepared by evaporating benzene from a mixed solution of PS and TBA, with subsequent pumping of the film in vacuum (10^{-3} Torr) for 4 days. The absence of tension in the prepared films was controlled using a polariscope. Photolysis was performed with an Hg high-pressure lamp. The desired irradiation wavelength was obtained using bandpass filters. The light intensity was calibrated by ferrioxalate actinometry [18]. The TBA contents in the samples were determined from the optical density of the longest wavelength absorption band ($\lambda = 393$ nm) (Fig. 1). The experiments were performed using PS films placed in
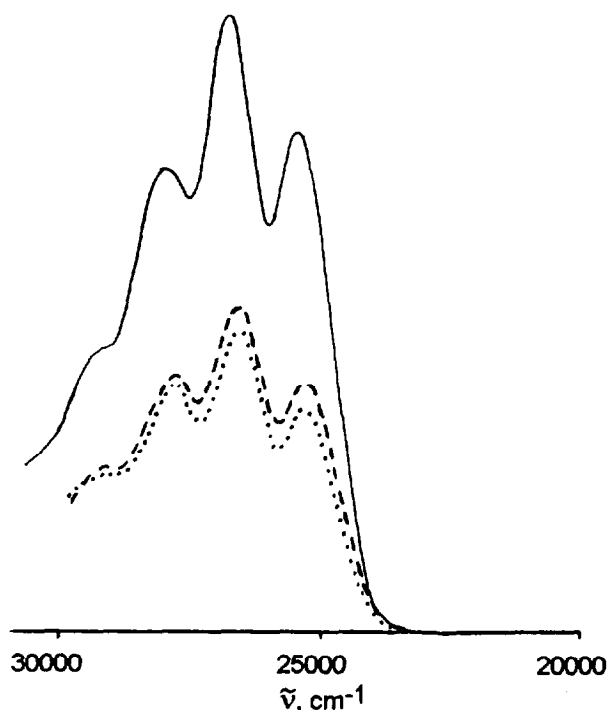
Fig. 1. Absorption spectra of TBA in PS at room temperature before photolysis (full line) and after photolysis with polarized light: polarizations of photolysing and probe light beams were perpendicular (broken line) and parallel (dotted line).

a quartz ampoule (diameter, 5 mm; square cross-section of the optical part).

Low-temperature experiments were carried out by placing ampoules in a transparent quartz Dewar vessel containing n-pentane; the temperature was kept constant within ± 2 °C.

For photolysis and spectrophotometry with polarized light, Glans prisms were used. A prism was installed in the path of the photolysing and probe light beams in front of the sample. The optical anisotropy was measured by the difference between the optical densities $D_{\perp}$ and $D_{\parallel}$ ($\lambda = 393$ nm), obtained at perpendicular and parallel mutual orientations of the photolysing and probe beam polarizations, and was characterized by the linear dichroism $d = (D_{\perp} - D_{\parallel})/(D_{\perp} + D_{\parallel})$. The concentration of TBA during photoselection was calculated from the magnitude of the average optical density of TBA, $D = (2D_{\perp} + D_{\parallel})/3$. The part of the remaining TBA molecules was defined as $\xi = D/D_0$.

3. Experimental results

During the photolysis of TBA in PS in air, the optical density of TBA falls to 5% of its original magnitude. The quantum yields of TBA depletion were calculated from the beginning of the TBA consumption kinetics and are presented in Table 1. After the termination of photolysis, the reverse thermal reaction is observed.

Table 1
Quantum yields of depletion of TBA during photolysis of the sample in air (ϕ) and in vacuum (ϕ_i), and the ultimate magnitudes of the TBA dichroism. λ_f is the wavelength of photolysing light. The values in parentheses indicate the magnitude of the dichroism for vacuum-treated samples

λ_f	ϕ	ϕ_i	d
313	0.10 ± 0.01	0.01 ± 0.002	0.00
365	0.047 ± 0.005	0.012 ± 0.002	$0.03 - 0.04$
405	0.034 ± 0.003	0.009 ± 0.01	$0.05 - 0.07$
			$(0.08 - 0.12)$

During the reverse process, only 15%–25% of the photodestroyed optical density of TBA is restored.

TBA photoisomerization in evacuated samples leads to a decrease in the quantum yield of TBA consumption and complete restoration of the original optical density of TBA (original denotes before photolysis). The "photolysis–thermal restoration" cycle in evacuated samples can be repeated many times without any loss of TBA or change in the kinetics of reaction (Fig. 2). No influence of oxygen on the reverse thermal reaction was detected: the kinetics of the thermal reaction in vacuum and air were identical for the samples photolysed in vacuum.

When the reaction was performed in a polyvinylbutyral film, which is optically transparent up to 220 nm, the growth of an absorption band at approximately 280 nm, typical of Dewar TBA [15,16], was observed during the course of photolysis.

Thus the reaction of TBA in PS results in photoisomerization into Dewar's product. The influence of oxygen on the behaviour of the system verifies that photo-oxidation proceeds together with TBA photoisomerization. Such reactions are characteristic of condensed aromatic compounds in PS [19]. As a result, the quantum yields of photoisomerization of TBA were measured in vacuum-treated samples and are presented in Table 1.

The photoisomerization reaction was also observed at low temperatures: 0–-80 °C. At liquid nitrogen temperature, no reaction was observed. In the temperature range $+20$–-80 °C, the quantum yields of TBA isomerization obey an Arrhenius dependence

$$\ln \phi = (0.3 \pm 0.1) - (2.95 \pm 0.05) \text{ kcal mol}^{-1}/RT$$

Photolysis with linearly polarized light induces the linear dichroism of the samples. The maximum magnitudes of the dichroism obtained in air for different wavelengths of photolysing light are presented in Table 1. The maximum dichroism was observed on irradiation at $\lambda = 405$ nm. For the evacuated samples at this wavelength, the dichroism was greater than that in air: 0.08–0.12 and 0.05–0.07 respectively.

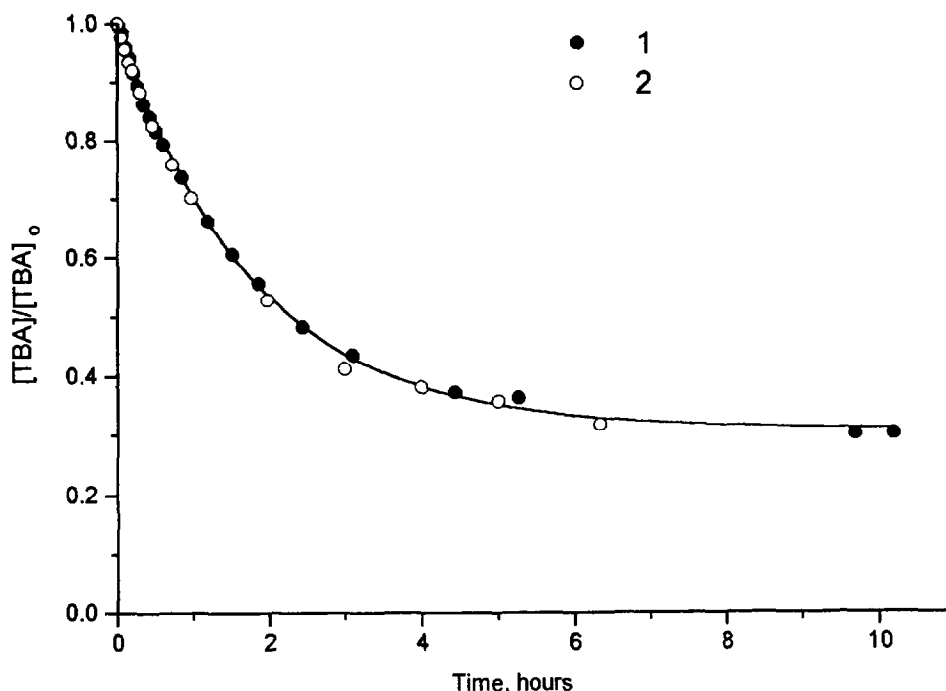To explain the experimental results, we must answer the following questions.

Fig. 2. The kinetics of photoisomerization of TBA in PS in evacuated samples on irradiation with light of $\lambda = 405$ nm. 1 and 2 represent the first and second photolysis of the same sample separated by the reverse thermal reaction with complete restoration of TBA quantity.

(1) How does the thermal reversibility of the reaction affect the magnitude of the ultimate dichroism and how does this magnitude depend on the rate constant of the thermal reaction?

(2) How does the thermal rotation ability of reactive molecules affect the observed magnitude of the TBA absorption dichroism?

(3) Does the inclusion of the reverse thermal reaction and thermal rotation of the reactive molecules allow to describe the experimental kinetics of TBA photo-isomerization, accumulation of optical anisotropy during photoselection and the small magnitudes of TBA dichroism which were obtained (in ideal systems the dichroism is equal to unity [8–10]) to be explained?

(4) Why is the TBA dichroism obtained in air less than that for the evacuated samples.

To answer these questions, three models of photo-selection in thermoreversible photochemical reactions were considered: (i) without thermal rotation of the reactive molecules; (ii) with account taken of the mobility; (iii) with the simultaneous presence of a photochemical side reaction (in our system, the photo-oxidation of TBA by oxygen in air).

4. Model

Four assumptions are considered.
(1) A chemical reaction takes place in accordance with the scheme

$$A \underset{kT}{\overset{h\nu}{\rightleftharpoons}} B$$
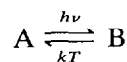
(2) Initially, reactive molecules are randomly oriented.

(3) The extinction coefficient tensor (ECT) of reacting molecules is axial: $\epsilon_x = \epsilon_y \neq \epsilon_z$.

(4) The orientation of a molecule of the initial compound is assumed to be completely restored during the reverse reaction.

Photolysis is carried out with linearly polarized light. The optical densities at the photolysis wavelength are controlled to be small enough for the intensity of the irradiating light to be accepted as constant over the entire thickness of the sample.

The orientation distribution function of the molecules with regard to the axial ECT is described via an orientational distribution function $\rho(\beta,t)$, where $\rho(\beta,t)d\beta$ is the fraction of the molecules with orientations in the interval β to $\beta + d\beta$. β is the angle between the orientation of the main axis of the molecular ECT and the direction of photolysing light polarization. The optical densities $D_\perp$ and $D_\parallel$ and the fraction of the remaining compound ξ are defined as [10]

$$D_\parallel(t) = D_0 \int_0^\pi \epsilon_\parallel(\beta)\rho(\beta, t) \, d\beta \qquad (1a)$$

$$D_\perp(t) = D_0 \int_0^\pi \epsilon_\perp(\beta)\rho(\beta, t) \, d\beta \qquad (1b)$$

$$\xi(t) = \int_0^\pi \rho(\beta, t)\, d\beta \tag{1c}$$

where D_0 is the optical density of an isotropic sample before the start of photolysis.

$$\epsilon_{||} = 1 + 2P_2(\cos\beta)(\epsilon_z - \epsilon_x)/3 \tag{2a}$$

$$\epsilon_\perp = 1 - P_2(\cos\beta)(\epsilon_z - \epsilon_x)/3 \tag{2b}$$

where ϵ_z and ϵ_x are the dimensionless extinction coefficients ϵ'_z/ϵ and ϵ'_x/ϵ respectively, $\epsilon = (\epsilon'_z + 2\epsilon'_x)/3$ where ϵ'_x and ϵ'_z are the real components of ECT [10] and $P_2(\cos\beta) = (3\cos\beta - 1)/2$ is the second Legendre polynomial.

In the absence of the thermal rotational mobility of the reactive molecules (in the "rigid medium" approximation), the system behaviour is defined by the set of equations

$$d\rho^A/d\tau = -\epsilon_{||}\rho^A + k\rho^B \tag{3a}$$

$$d\rho^B/d\tau = \epsilon_{||}\rho^A - k\rho^B \tag{3b}$$

where ρ^A and ρ^B are the orientational distribution functions for the molecules of an initial compound A and the reaction product B, τ is a dimensionless time ($\tau = 2.303t\phi I_0 l\epsilon/v$), k is a dimensionless constant of the thermal reaction ($k = vK/2.303\phi I_0 l\epsilon$), K is a real constant of the thermal reaction, ϕ is the quantum yield of the photochemical reaction, l is the optical path length in the specimen, v is the volume of the sample and I_0 is the intensity of the irradiating light.

The relations for the steady state values ξ^S, $D_\perp{}^S$, $D_{||}{}^S$ and the dichroism of the optical absorption d^S, obtained as a solution of Eqs. (3a) and 3(b), are as follows

$$\xi^S = \begin{cases} \dfrac{k}{(\epsilon_z - \epsilon_x)}\arctan(1/a), & \epsilon_z > \epsilon_x \tag{4a} \\[2ex] \dfrac{k}{2(\epsilon_x - \epsilon_z)}\ln\left(\left|\dfrac{1+a}{1-a}\right|\right), & \epsilon_z < \epsilon_x \tag{4b} \end{cases}$$

where $a = [(k + \epsilon_x)/|\epsilon_z - \epsilon_x|]^{1/2}$

$$D_\perp{}^S/D_0 = k(1 - \xi^S); \quad D_{||}{}^S/D_0 = (3 + 2k)\xi - 2k \tag{5a}$$

$$d^S = 3(\xi^S - D_\perp{}^S/D_0)/(3\xi^S + D_\perp{}^S/D_0) \tag{5b}$$

Thus the knowledge of k and the assumption that molecules A absorb light in one direction ($\epsilon_z = 3$, $\epsilon_x = \epsilon_y = 0$) enable a rough estimation to be made of the highest limit of dichroism that can be obtained in a thermoreversible system with a given magnitude of k. The magnitude of the ultimate or steady state dichroism for the reversible reactions rapidly decreases with an increase in the constant of the reverse reaction (Fig. 3). Such an estimation will be more precise if
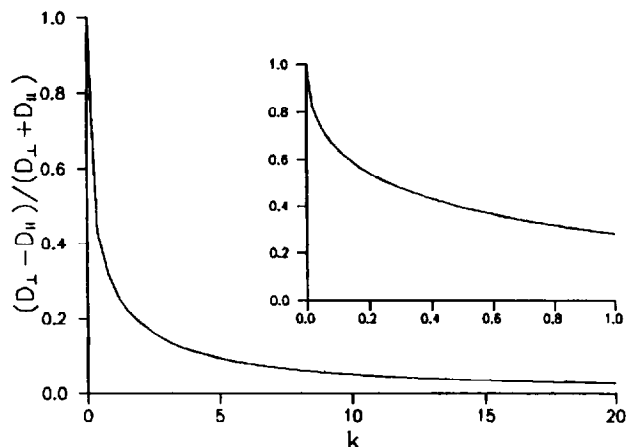

Fig. 3. Theoretical dependence of the ultimate magnitude of the dichroism on the constant of the reverse thermal reaction for photoselection conditions in the reaction $A \xrightarrow{h\nu} B$, $B \xrightarrow{kT} A$ in rigid media.

the magnitudes of the ECT components are known. However, the steady state dichroism obtained in such a manner must be considered with caution since during photolysis, in thermoreversible reactions, the dichroism passes through a maximum. The steady state magnitude may not be achieved during the time of the experiment. Therefore the calculation of the kinetics of dichroism enrichment is necessary for a thermoreversible reaction.

In order to account for the influence of a photochemical side reaction on the kinetics of dichroism accumulation during photoselection, the supplementary stage $A \to h\nu \to C$ was included in our model.

The system of equations describing the photoselection of a substance A in this situation appears as

$$d\rho^A/d\tau = -(1 + u)\epsilon_{||}{}^A\rho^A + k\rho^B \tag{6a}$$

$$d\rho^B/d\tau = \epsilon_{||}{}^A\rho^A - k\rho^B \tag{6b}$$

where $u = \phi_2/\phi_1$ and ϕ_2 and ϕ_1 are the quantum yields of the photochemical reactions $A \to C$ and $A \to B$ respectively; $\tau = 2.303t\phi_1 I_0 l\epsilon/v$.

The calculated reaction kinetics and dichroism accumulation are given below. It should be noted that the photochemical side reaction leads to an increase in the dichroism magnitude. This is induced by the relative decrease in the influence of the thermal reverse reaction.

Therefore the thermal reverse and side photochemical reactions have an opposite influence on the magnitude of the light-induced dichroism: the former reduces and the latter enhances the dichroism.

It is known that guest molecules in polymer matrices show a thermal rotational ability with correlation times within the range of the duration of the photochemical experiments [2,6]. This may affect the magnitude of the light-induced dichroism.

In the present work, the mechanism of molecular rotational mobility is considered within the context of

two models: non-correlated jumps and free rotational diffusion.

In general, the kinetics of photoselection for thermoreversible photoisomerization can be described by the equations

$$d\rho^A/d\tau = F^A(\beta, \tau) - \epsilon_\| \rho^A + k\rho^B \qquad (7a)$$

$$d\rho^B/d\tau = F^B(\beta, \tau) + \epsilon_\| \rho^A - k\rho^B \qquad (7b)$$

where $F^A(\beta,\tau)$ and $F^B(\beta,\tau)$ describe the thermal rotation of molecules of the initial compound A and the product of the reaction B in accordance with a rotational mechanism.

The model of non-correlated jumps proposes that the molecule loses its orientation by a rotational jump through an arbitrary angle, jumps through different angles being equally probable. So, the $F(\beta,\tau)$ members in Eqs. (7a) and (7b) appear as

$$F(\beta, \tau) = \kappa\rho + \kappa\tau\tau_0 + \kappa\rho_0\left(\int_0^\tau \rho \, d\beta - \rho\right)$$

where κ is the molecular jump probability per unit time. The solution of Eqs. (7a) and (7b) can be found by expansion of the orientational distribution function in terms of a Fourier sequence [20].

In the model of rotational diffusion, the molecular rotation is considered as a rotational diffusion of spherical particles in an isotropic medium with the absence of external forces. In this case, the member describing the change in the molecular orientation appears as [21]

$$F(\beta, \tau) = G\nabla^2\rho$$

where G is the coefficient of rotational diffusion of the molecule and ∇^2 is the Laplace operator in Euler coordinates. The solution of Eqs. (7a) and (7b) is found by expansion of ρ in terms of the Legendre polynomials.

5. Discussion

The experimental magnitudes of the TBA ECT components were determined in Ref. [22]: $\epsilon_z = 2.06$ and $\epsilon_x = 0.47$.

The reverse thermal reaction and relaxation of the optical anisotropy of TBA have been investigated previously [6,23]. The kinetics of the reaction are monoexponential. In the temperature range 20–50 °C, the rate constant of the reaction (K) obeys an Arrhenius dependence

$$\ln K = (27 \pm 1) - (22.1 \pm 0.3) \text{ kcal mol}^{-1}/RT$$

The relaxation of TBA anisotropy, described by the time evolution of $(D_\perp(t) - D_\|(t))$, obeys a monoexponential law [6]. Rotational correlation times (τ_c) for reacting molecules were obtained in Ref. [6] as 2×10^4 s at room temperature.

This enables a theoretical calculation to be made of the reaction kinetics and accumulation of dichroism during the photoselection of TBA, which can be compared with the experimental values. The exponential kinetics of the thermal reaction allow Eqs. (3)–(7) to be used for the analysis of photoselection in a given system. (Frequently, the kinetics of thermal reactions in solids do not obey simple monoexponential decay [24,25]. In this case, Eqs. (3)–(7) cannot be applied.)

The kinetics of the reaction and the accumulation of dichroism for the irreversible photochemical reaction under the conditions of photoselection in a "rigid medium" are shown in Fig. 4 (full lines). The calculated curves differ significantly from those obtained experimentally.

The consideration of the thermal reaction (constant of the thermal reaction is $5 \times 10^{-5} \text{ s}^{-1}$ [6]; dimensionless $k = 0.28$) results in a considerable improvement in the description of the experimental data (Fig. 4, broken lines).

The consideration of the thermal mobility of the reacting molecules further improves the description of the experiment. The rotation of the molecules was considered in terms of the models of uncorrelated jumps and rotational diffusion in accordance with Eqs. (7a) and (7b). The results of the calculations according to both models coincide and adequately describe the experiment (Fig. 4, dotted lines). It should be noted that, as in the thermal processes [6,26], in the photochemical reactions the models of molecular rotation cannot be distinguished by optical methods.

Although the consideration of the molecular rotational mobility improves the description of the experimental data, it does not improve the description of the experimental data as markedly as the consideration
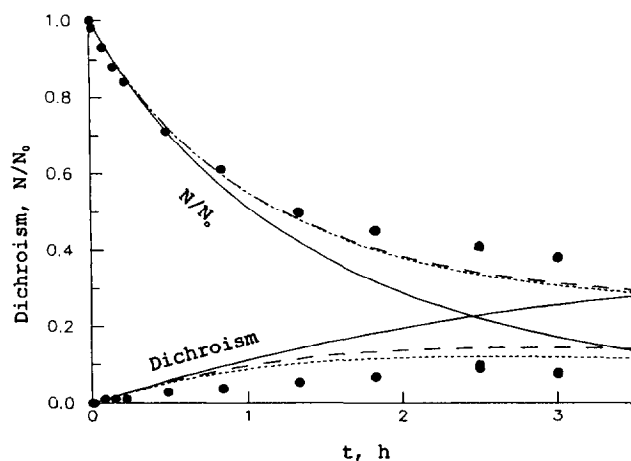

Fig. 4. Calculated kinetics and dichroism accumulation during photoselection in the reactions: $A \xrightarrow{h\nu} B$ in rigid media (full lines), $A \xrightarrow{h\nu} B$, $B \xrightarrow{kT} A$ in rigid media (broken lines), $A \xrightarrow{h\nu} B$, $B \xrightarrow{kT} A$ with consideration of the thermal rotation of molecules A and B (dotted lines). Filled circles represent the experimental data.

of the reverse thermal reaction. The results presented in Fig. 4 and Table 2 also demonstrate this. Therefore the most significant factors which determine the magnitude of TBA dichroism during the photoisomerization of TBA in PS under photoselection conditions are the ECT components and the reverse thermal reaction.

The remainder of the deviation of the theoretical calculations from the experimental results may be caused by the partial non- equivalence of the photoisomerization kinetics. The non- equivalence must decrease both the degree of conversion and the magnitude of TBA dichroism. The molecular recoil at the instant of the reaction and the deviation from ECT axiality may also contribute to the deviation of the theoretically calculated magnitudes from the experimental values.

However, the factors discussed above do not explain why the TBA optical absorption dichroism produced for evacuated samples is higher than that in air. On photolysis in air, the photo- oxidation reaction dominates over the photoisomerization of TBA: $\phi_2/\phi_1 \approx 3$, where ϕ_2 and ϕ_1 are the quantum yields of TBA photo-oxidation and photoisomerization respectively. The calculated kinetics of TBA consumption and the accumulation of dichroism for samples in air and in vacuum (according to Eqs. (6a), (6b) and (3a), (3b) proposed above) are given in Fig. 5. These calculations show that, in the presence of an effective photochemical side

reaction, the observed dichroism should be approximately 1.5–2.5 times greater than the value without it. However, the opposite effect is observed experimentally. We propose that this inconsistency can be explained by the mechanism of photo-oxidation. The excited triplet state of an aromatic compound and the excited singlet state of oxygen are known to take part in the process of photo- oxidation of aromatic compounds in a polymeric matrix [24]. At the experimental TBA concentration of 10^{-2}–10^{-3} M, the migration of the triplet state excitation energy [27], which violates the photoselection process, is possible [28–30]. Moreover, the selection process is also violated substantially at the oxidation step. Singlet oxygen formed as an intermediate may react not only with a donor molecule of TBA but also with any other neighbouring molecules. Thus, in contrast with the theoretical predictions, the photo-oxidation reaction appears to reduce dichroism.

Acknowledgement

Table 2
Comparison of the theoretically calculated ultimate magnitudes of the TBA dichroism with the experimental magnitudes obtained in PS at room temperature

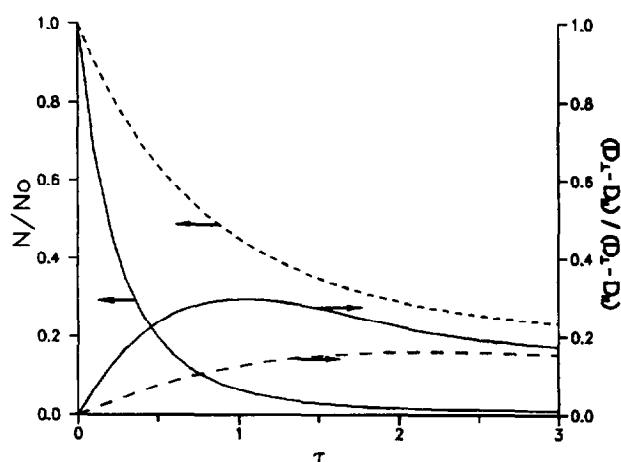|	$k = 0$	$k = 0.28$
$\epsilon_x = \epsilon_y = 0$, $\epsilon_z = 3$	1.0	0.49
$\epsilon_x = \epsilon_y = 0.47$, $\epsilon_z = 2.06$	0.46	0.12
Experiment	–	0.09–0.12

Fig. 5. Calculated kinetics and dichroism accumulation during photoselection in rigid media in the reactions: $A \xrightarrow{h\nu} B$; $B \xrightarrow{kT} A$, $A \rightarrow h\nu \rightarrow C$, full line; $A \xrightarrow{h\nu} B$; $B \xrightarrow{kT} A$, broken line ($\epsilon_z^A = 2.06$, $\epsilon_x^A = 0.47$, photolysing light is linearly polarized, $k = 0.2$).

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